IDECAT Integrated Design of Catalytic Nanomaterials for a Sustainable Production

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Synergetic and precursor effects in propane total oxidation over Cu- and Ce-based catalysts

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Introduction

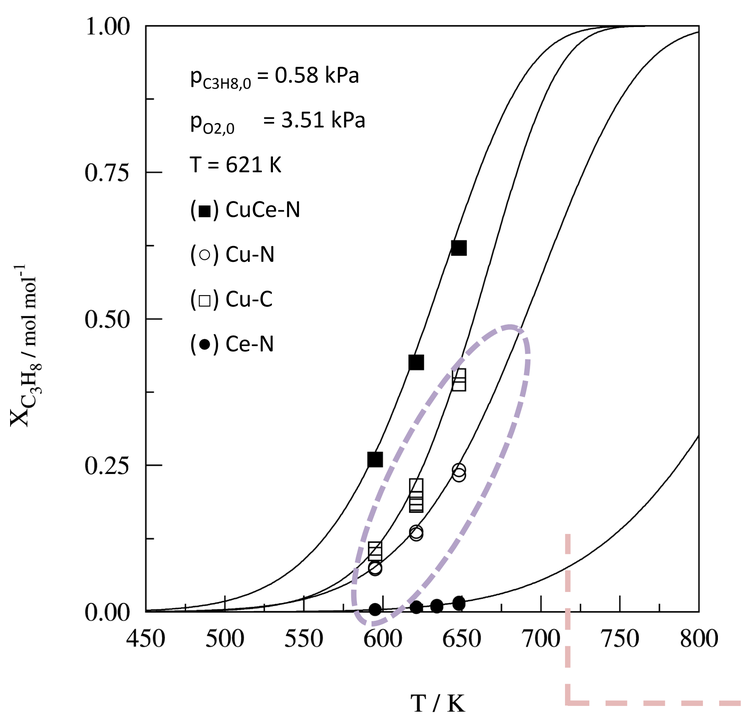
Volatile organic compounds (VOC's) exhibit a significantly high vapour pressure at ambient conditions. These VOC's are responsible for increased levels of ozone in the troposphere and for_ozone depletion in the stratosphere. According to Theloke and Friedrich, one third of all emitted VOC's are alkanes [1]. Emissions from both stationary and non-stationary sources are subjected to an ever stricter legislation, due to an increasing environmental awareness. Catalytic oxidation offers the advantage over thermal incineration that these VOC's can be removed from effluent streams in low concentrations and at relatively low temperatures [2]. This paper describes the total oxidation of propane as model reaction over Cu- and Ce-based catalysts by means of steady-state experiments.

Acquisition of experimental data

Four catalysts are used: a $CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$, catalyst, formally denoted as CuCe-N, synthesized by impregnation of a $\gamma\text{-}Al_2O_3$ carrier with precursors $Cu(NO_3)_2$ and $Ce(NO_3)_4$; catalysts Cu-N and Cu-C are made by impregnation of $\theta\text{-}Al_2O_3$ with $Cu(NO_3)_2$ and $CuCO_3$; a Ce-N catalyst is obtained by impregnation of a $\gamma\text{-}Al_2O_3$ carrier with $Ce(NO_3)_4$.

These four catalysts are tested in the total oxidation of propane using a conventional plug flow reactor with a propane and oxygen inlet partial pressure of 0.58 kPa and 3.51 kPa at three temperatures: 595, 621 and 648 K. For sample Ce-N, an extra temperature level of 634 K is applied. The space time is varied up to 570 kg_{cat} s mol^{-1}.

Results



The experimental data are regressed by a Mars-van Krevelen (MVK) model. This model corresponds to a reduction step in which propane reacts with a single oxidized site and with a reoxidation step by gas phase oxygen, involving a single reduced surface site.

$$r = \frac{k_{O_2} k_{C_3H_8} p_{O_2} p_{C_3H_8}}{k_{O_2} p_{O_2} + 5 k_{C_3H_8} p_{C_3H_8}}$$

$$E_{app}^{calc} = \frac{\partial \ln r}{\partial T} RT^2$$

$$E_{app}^{calc} = \theta_{O^*} E_{C_3H_8} + (1 - \theta_{O^*}) E_{O_2}$$

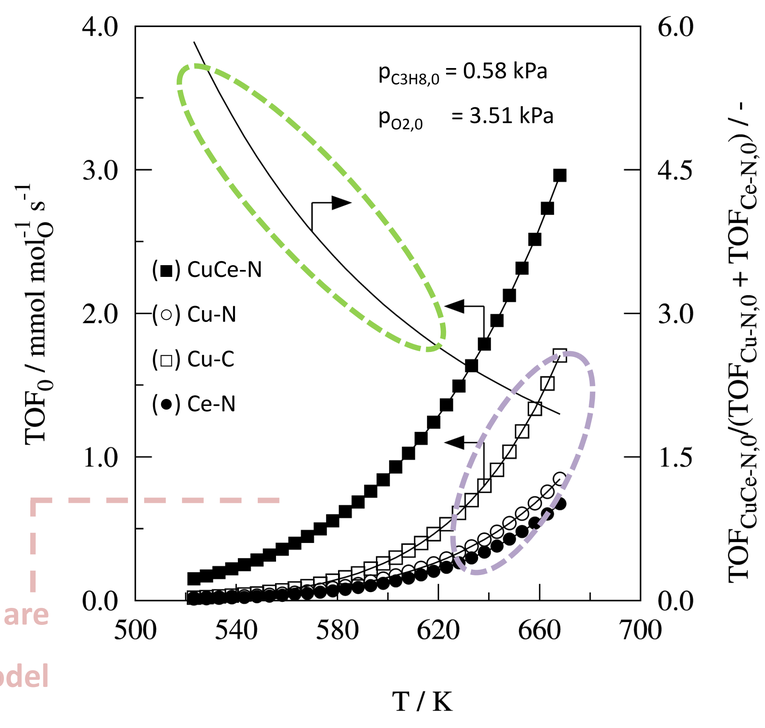
$$E_{app}^{obs} \doteq E_{app}^{calc}$$

$$\theta_{O^*} = \frac{E_{app}^{obs} - E_{O_2}}{E_{C_3H_8} - E_{O_2}}$$

obtained from regression of experimental data with power law model [3]

lines are calculated with MVK model

catalyst	$k_{O2,0}$ / mol mol_O^{-1} s^{-1} Pa^{-1}	E_{O2} / kJ mol^{-1}	$k_{C3H8,0}$ / mol mol_O^{-1} s^{-1} Pa^{-1}	E_{C3H8} / kJ mol^{-1}	θ_{O^*} / -
CuCe-N	$(2.01 \pm 0.65)\ 10^{-1}$	47.2 ± 3.5	$(3.29 \pm 1.07)\ 10^{+0}$	74.9 ± 5.5	0.45 ± 0.32
Cu-N	$(2.46 \pm 0.72)\ 10^{-1}$	50.8 ± 2.4	$(1.39 \pm 0.41)\ 10^{+0}$	78.5 ± 3.7	1.11 ± 0.20
Cu-C	$(1.14 \pm 0.17)\ 10^{+1}$	72.4 ± 2.9	$(6.27 \pm 0.91)\ 10^{+1}$	95.3 ± 3.8	0.75 ± 0.28
Ce-N	$(2.11 \pm 0.62)\ 10^{+0}$	77.9 ± 4.4	$(2.97 \pm 0.87)\ 10^{+2}$	102.5 ± 5.9	0.17 ± 0.23



Lines and points are calculated with MVK model

Conclusions

A $CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ catalyst synthesized by impregnation with nitrate precursors is the best catalyst for the oxidation of propane from a series of four copper oxide and ceria-based catalysts. **Whereas the reduction step seems to be the most critical step in the reaction mechanism on Cu-based catalysts, it is the reoxidation that is critical on a CeO_2 based catalyst.** A mixed oxide $CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ allows combining the good characteristics of both types of oxides in a synergetic way. A precursor effect is observed by using two copper oxide catalysts, made by impregnation of $Cu(NO_3)_2$ and $CuCO_3$ on $\theta\text{-}Al_2O_3$. The latter catalyst shows higher propane conversion as well as TOF.

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Acknowledgements

This work was performed in the framework of a Concerted Research Action (GOA), financed by Ghent University. The project 1.5.201.07 sponsored by the FWO-Vlaanderen is also gratefully acknowledged. This work has also partly been performed within the IAP-PAI framework sponsored by the Belgian Science Policy.

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